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Heterogeneous reactivities of excited states

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Multiphase photosensitization in atmospheric aerosols has recently been proposed to induce a new oxidation pathway in the formation of secondary pollutants. Biomass burning, as an important source of aromatic carbonyls and HUmic-LIke Substances (HULIS), may initiate photosensitized aerosol multiphase oxidation, however the understanding of this process is still at its beginning. Limited studies have shown that direct photosensitized oxidation of Vanillin (VL) and 4-carboxybenzophenone (4-CB) form triplet excited states(3C*) leading to aqueous secondary organic aerosol (aqSOA) formation. Currently, the heterogeneous process of excited states is unclear.

In this study, we focused on the reactivity of triplet-excited states with gas phases (O_3, SO_2 and NO_x) and VOC_S, using a Wetted-Wall Flow Tube (WWFT) in the dark and in the UVB (300~340nm), we investigated the reactivity of two biomass burning model compounds (aromatic carbonyls), VL and 4-CB with ozone. The reactions were characterized based on O_3 decay kinetics, detected uptake, and the effect of photosensitizer concentration and temperature. It was confirmed that the uptake on VL and 4-CB containing solutions under UVB and O_3 exposure is significantly enhanced. The uptake coefficient (γ) of O_3 linearly increased with VL at low concentration (0-15.2 $mg.L^{-1}$), and is eventually independent on VL concentration afterwards (15.2-152 $mg.L^{-1}$), the steady-state uptake coefficient is $(1.05 \pm 0.14)\times10^{-5}$. VL can react with O_3 in the dark, but the reaction of 4-CB hardly occurs. Meanwhile, the same method was applied to measure the water-soluble samples (HULIS) in realistic conditions. With ambient sample concentration of 0.29 $\mu g.m^{-3}$ to 1.17 $\mu g.m^{-3}$, it also leads to an enhancement under irradiation.

Overall, this study indicates that the photochemical process of VL and 4-CB is driven by excited states, causing the decay of O_3. The ambient samples also exhibited photosensitization similar to biomass burning model compounds, proving the extensibility of the mechanism.

This work reveals the importance of photosensitized reactions in the tropospheric condensed phase (i.e., cloud droplets and aerosols). It is a key for us to better understand and respond to the impact of biomass burning particulate matter on climate change.